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Use of energy-filtered photoelectron emission microscopy and Kelvin probe force microscopy to visualise work function changes on diamond thin films terminated with oxygen and lithium mono-layers for thermionic energy conversion

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Abstract: Kelvin probe force microscopy (KPFM) and energy-filtered photoelectron emission microscopy (EF-PEEM) with vacuum UV (VUV) excitation have been used to study the work function of *p*-type diamond films treated to exhibit a negative electron affinity (NEA) surface. NEA was generated by a lithium-oxygen monolayer termination. This monolayer was achieved in two different ways: thermally evaporated films 50 nm thick were either treated by *in situ* vacuum annealing or by a subsequent water wash. The work function values obtained from these samples by EF-PEEM were compared with KPFM measurements to establish which of the two fabrication techniques was most effective in activating a NEA surface. The washing method was shown to be more effective and the work function values obtained by the two techniques were comparable, as they showed the same work function peaks at 4.54 eV in their respective histograms. It was found that neighbouring polycrystalline facets could show a large variation in work function of up to 400 meV.

Keywords: diamond; chemical vapour deposition; negative electron affinity; Kelvin probe force microscopy; energy-filtered PEEM; work function; energy conversion; thermionic emission; nanotechnology; surface functionalisation.

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1 Introduction

A thermionic diode energy converter consists of a hot cathode that emits electrons towards a cooler collector, these two being separated by a vacuum gap that may contain an ionisable gas. Electrons absorbed at the collector give up kinetic energy in the form of heat, and the potential energy, which they also carry, is used to do work in an external electrical load. In this way, heat is converted into electrical power. This type of energy converter is ideally suited for energy-harvesting applications that employ sources of concentrated heat such as solar, geothermal or combustion. Like thermoelectric and photovoltaic devices, it operates without any moving parts, but unlike these other technologies its performance improves significantly with temperature.

Recently, semiconducting diamond has been considered as a candidate material for low temperature thermionic energy converters [1,2]. For this application, the diamond surface needs to be activated to exhibit a NEA. In the presence of a NEA, hot electron carriers, which have thermalised to the bottom of the conduction band minimum, are emitted with a total energy that is higher than the vacuum potential barrier between emitter and collector, thus allowing the thermionic converter to produce a voltage output.

The NEA condition is produced when the vacuum energy level lies below the conduction band minimum. Its value can be determined with the following formula:

$$\text{NEA} = \phi + (E_\text{F} - E_\text{VBM}) - E_\text{BG}$$

where ϕ is the work function of the diamond surface, E_F the energy of the Fermi level, E_VBM the energy of the valence band maximum and E_BG is the value of the energy band gap. All the magnitudes are measured in eV. E_F, E_VBM and E_BG are fixed parameters for a given semiconductor with a certain doping type and concentration. The surface work function, on the other hand, can be modified relatively easily and can be used to change the value of NEA. Hence, to monitor the value of the work function, it becomes necessary to find adequate techniques that provide accurate and reliable readings of the mentioned magnitude.

As the work function is a surface-dependent property, it is possible to tune the value of the work function by surface modification on certain materials. In the case of diamond, it is the only Group 14 element whose surface does not exhibit a native oxide. This fact allows the surface to be functionalised with species that would not intuitively be regarded as technologically useful. But these can indeed have a significant impact on the work function of the diamond.

A NEA surface may be generated by terminating the surface of diamond with hydrogen [3,4]. However, it is found that this NEA condition is not stable at elevated temperatures due to hydrogen desorption, making it problematic to use in vacuum thermionic converters operating above red heat.

Ab initio modelling conducted previously [5] and experiments by our group have demonstrated the potential of an oxygen-lithium terminated surface for enhancing the low temperature operation of thermionic electrodes formed from diamond. This surface termination reduces the diamond work function and exhibits a large NEA [6,7] on both *p*- and *n*-type diamond, and it is stable at temperatures in excess of 1100$^\text{o}$C [8]. Thermionic emission studies on *n*-type diamond indicated that emission was enhanced with oxygen-lithium compared with that with hydrogen termination. However, XPS studies [9] have suggested that surface coverage of the oxygen-lithium termination on diamond is much less than 50%.

To characterise the functionalised diamond surface, two complementary techniques were identified that could provide the means to visualise the variation in work function across the surface of functionalised diamond. These are: EF-PEEM [10] with VUV excitation and ultra high vacuum KPFM.

Kelvin probe force microscopy is a non-contact AFM technique that provides topographic information and contact potential difference (CPD) contrast of a sample surface with nanometre lateral resolution and an energy resolution of tens of millivolts. It has its origins in the Kelvin method that was originally developed by Lord Kelvin by the end of the 19th century. In this method, two conducting plates corresponding to sample and probe are placed in a parallel capacitor configuration with a small spacing. Then, the probe plate is vibrated at a known frequency, ω. The change in distance between the plates causes a capacitance variation and that produces an alternating current I in the circuit that interconnects the plates. If a DC voltage bias V_{CPD} is applied on one of the plates so that the current becomes zero, the bias voltage will correspond with the value of the CPD of the two materials.

$$I(t) = V_{\mathrm{CPD}} \cdot \omega \cdot \Delta C \cdot \cos \omega t$$

With advances in atomic force microscopy (AFM) technology, in the early 1990s, Nonnenmacher et al. [11] developed the KPFM technique, which can perform a surface CPD mapping with nanometre lateral resolution. KPFM is a combination of the Kelvin method with a non-contact AFM. The two plates are replaced in this case by the sample and the cantilever tip, and a bias DC bias voltage is used to compensate the CPD between sample and tip. As a controlling parameter, the current between tip and sample is replaced by the electrostatic force sensed by the cantilever. This makes KPFM highly sensitive to small changes in CPD.

KPFM can be operated in two modes, namely amplitude modulation (AM-KPFM) or frequency modulation (FM-KPFM) [12]. The former is sensitive to the electrostatic force on the surface whereas the latter is sensitive to the gradient of the electrostatic force. This fact makes FM-KPFM more sensitive to changes in CPD and therefore it achieves better lateral resolution. The FM-KPFM mode works on a two-pass basis. In the first pass, the cantilever is operated in non-contact mode and it detects the topography. Then, the second pass operates in a lift-mode, whereby the tip is lifted from the surface and scans the already known topography searching for changes in CPD. This mode can also operate on a single pass mode where the CPD is detected at the same time as topography. KPFM measures the CPD between two materials, which is in essence the difference between the work function of the tip and that of the sample.

$$\mathrm{CPD} = \frac{1}{e}(\phi_{\mathrm{tip}} - \phi_{\mathrm{sample}})$$

However, this magnitude can be influenced by a number of factors. The formation of oxide layers in the surface, the environment in which the measurements are taken (air humidity) or the presence of adsorbed molecules on the sample and the tip can create surface dipoles that influence the final CPD value. In this study, the property of interest is the work function of the sample, so all of the mentioned parameters were controlled to minimise their influence to be as close as possible to the real value of the work function (see Section 2).

Energy-filtered PEEM combines an electrostatic photoemission electron microscope (PEEM) column, with an imaging electron spectrometer. A suitable way to perform reliable, high resolution XPS spectromicroscopic imaging with laboratory sources is to use, as imaging spectrometer, a double hemispherical analyser in the so-called NanoESCA instrument described previously [10,13]. Such an energy filter in XPEEM provides high transmission due to aberration compensation, which is accomplished by configuring two hemispherical analysers in series so that the aberration effects of the first exactly cancel those in the other.

The energy-filtered PEEM provides full-field photoelectron imaging at large fields of view – tens of microns. In the case of work function, measurements are provided from spectroscopic imaging with secondary electrons, in the intense threshold regions of the photoemission spectrum. In these conditions, the lateral resolution is less than 150 nm and the sensitivity to work function changes is 20 meV.

In principle, different photon excitation sources can be used, from soft X-ray synchrotron radiation and Al Kα X-rays (XPEEM), to lower energy sources in the UV with Hg ($h\nu = 4.9$ eV) or the VUV range with He I ($h\nu = 21.2$ eV).

To map the work function, the sample is illuminated with He I or Hg sources while a sequence of images is taken across the photoemission threshold at increasing energy ($E - E_F$) of the secondary photoelectrons, E_F being the Fermi level of the sample. This provides a set of images depicting the emission intensity $I(x, y, E - E_F)$. Then, for each pixel $I(x, y)$, the local work function is calculated by fitting the photoemission threshold $I(E - E_F)$, equivalent to the local work function, using:

$$I(E - E_{\mathrm{F}}) = \frac{I_{\max}}{2}\,\mathrm{erfc}\left(\frac{\phi - (E - E_{\mathrm{F}})}{\sigma\sqrt{2}}\right) + I_{\mathrm{off}}$$

where $I_{\max}$ is the maximum intensity of the spectrum of each pixel, ϕ is the local work function, I_{off} is the intensity offset and σ is the standard deviation of the Gaussian due to the energy broadening of the imaging spectrometer, at the pass energy used.

The work function value for each pixel can be used to build up a greyscale image that displays the variation in the magnitude of the work function across the sample surface. The EF-PEEM provides a large number of work function data points that allow an accurate estimation of the position of the work function peaks and the average work function value on the sample.

In this report, we present a preliminary examination of the surface work function of *p*-type diamond with an oxygen-lithium functionalised surface employing EF-PEEM and UHV KPFM. These techniques both produce maps of the variation of surface work function, but at lateral scales and spatial resolutions that are quite different. However, both techniques allow the work function measurement to be related with the morphology of the diamond surface such as crystallographic orientation, therefore enabling the possibility of relating low work function areas to the effectiveness of the surface functionalisation.

The aim of this study was to establish the dependence of work function on the type, number and quality of polycrystals exhibiting a given crystallographic orientation on the surface of the diamond film. Such information would help to optimise its morphology enhancing the coverage of oxygen-lithium on the diamond film surface to obtain a low work function.

2 Experimental

2.1 Chemical vapour deposition

Two boron-doped *p*-type diamond films were grown on a 10 × 10 mm *p*-type single crystal Si substrate by the method of hot filament chemical vapour deposition (HFCVD) [14] using a linear array of rhenium filaments. The substrate was manually abraded using 1–3 μm graded diamond powder (Diadust, Geneva, Switzerland) to provide a seed layer for diamond growth. The deposition time of both films was 3 h, giving a total film thickness of 3 μm. The temperature of the substrate was approximately 850ºC using a gas mixture of $H_2/CH_4/B_2H_6$. The flow rates of the gases were, respectively, 200 sccm, 2 sccm, 0.2 sccm. The pressure inside the HFCVD system was kept at 20 Torr during the deposition process.

The diamond samples were then exposed to atomic oxygen in an ozone plasma cleaner to remove any impurities from the surface and to form an oxygen-terminated diamond surface. This was followed by lithium deposition accomplished by evaporating lithium onto the oxidised diamond surface. Then, the two samples were processed by different methods to remove the excess lithium and create a monolayer of the metal atoms coordinated with oxygen atoms on the diamond surface. Sample PCMD (Figure 2(A)) was annealed under vacuum at 850ºC immediately after lithium deposition, whereas sample PCMD2 (Figure 2(B)) was removed from vacuum without annealing and washed in deionised water.

2.2 Kelvin probe force microscopy

KPFM measurements were performed using an Omicron UHV VT AFM scanning probe microscope (Omicron NanoTechnology GmbH, Taunusstein, Germany) at room temperature with a base pressure of 1.5×10^{-9} mbar. Once inside the chamber, the sample was annealed at 300ºC for 1 h to remove any undesired adsorbed impurities from the surface. KPFM was carried out using nanosensors PPP-NCSTAu gold coated cantilevers (Nanosensors, Neuchatel, Switzerland) operated in frequency modulation mode. The tip was annealed at 120ºC for 1 h once inside the system to eliminate any adsorbed impurities that could distort the measurements. The tip was calibrated every 24 h against HOPG (Highly oriented pyrolytic graphite) to ensure the stability of the work function of the tip. The HOPG ($\phi = 4.475$ eV) [15] calibration sample was cleaved in air and quickly introduced in the UHV chamber to avoid any contamination. Once inside the chamber, it was annealed at 120ºC for 1 h to eliminate any adsorbed molecules remaining on the surface that could distort the calibration.

2.3 EF-PEEM

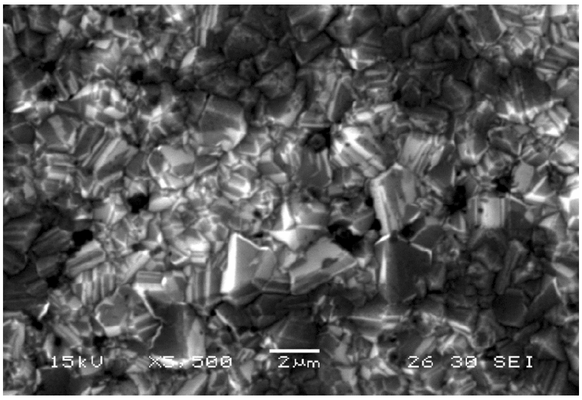
EF-PEEM measurements were performed at room temperature using a NanoESCA spectromicroscope (Omicron NanoTechnology GmbH, Taunusstein, Germany) with a base pressure of 5×10^{-11} mbar. Prior to measurements, the samples underwent annealing at 550ºC for 20 min to remove adventitious carbon contamination from the surface. Two light sources were used: a high pressure mercury discharge lamp ($h\nu = 4.9$ eV) and a He I cold cathode lamp ($h\nu = 21.2$ eV). Photoelectron images series were acquired across the photoemission threshold of the secondary electron tail, from electron energies ranging from 2 eV to 7 eV, with energy steps of 25 meV and a field of view of 53 µm. The extractor voltage of the objective lens was 12 kV, creating a typical electric field at the sample surface of 6.67 kV/mm, which typically lowers the work function due to Schottky effect. Therefore, the derived work function is corrected to take account of the Schottky effect, by adding 0.098 eV to the calculated value of ϕ, obtaining the final work function value of the sample.

3 Results

3.1 Scanning electron microscopy

Figure 1 shows a scanning electron microscopy image of a boron-doped diamond film, sample PCMD. A range of different crystallographic orientations can be seen on the surface, where the size of the crystal facets varies from 1 µm to 2 µm. Overall, the morphology is similar to previously reported boron-doped diamond films with planar facets alternated with step-like structures across the surface [16].

Figure 1 SEM image of a boron doped *p*-type diamond film with lithium-oxygen surface termination



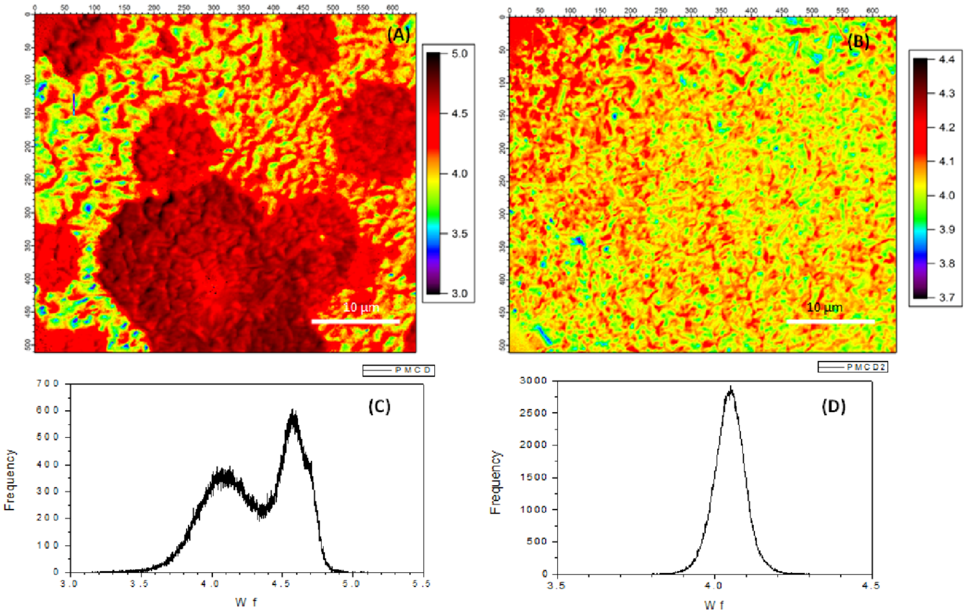
3.2 EF-PEEM

Figure 2(A) and (B) shows work function maps obtained with EF-PEEM of two boron-doped CVD diamond films treated with different lithium-oxygen surface functionalisation methods. These methods aim to produce a low work function across the diamond surface so a uniform coverage of the latter is necessary.

As can be seen in sample PCMD (Figure 2(A)), the vacuum annealing process does not produce a uniform surface. It presents circular patches of a variable size with a high work function that cover most of the surface, which is not desirable. On the histogram (Figure 2(C)), three peaks can be seen. The first one at 4.05 eV can be found on the second sample as well, whereas the other two peaks at 4.55 eV and 4.7 eV seem to belong to the circular patches with high work function where the surface functionalisation was unsuccessful.

The work function map for the washed sample, PCMD2 (Figure 2(C)), appears to be more uniform. This is confirmed by the smaller range of work function values (3.7–4.4 eV) shown in Figure 2(D) and a sharp peak at 4.05 eV. The data presented in Figure 2 suggests that the washing method employed in the sample PCMD2 performs better as it produces a surface with a more uniform spread of work functions, which also has an average value lower than the annealing method used in the sample PCMD.

Figure 2 (A) Work function image, VUV-energy filtered PEEM (He I, hv = 21.2 eV) of boron-doped, *p*-type polycrystalline diamond with Li-O functionalised surface formed by heating a lithium-coated surface, PMCD. (B) Work function image, VUV-energy filtered PEEM (He I, hv = 21.2 eV). (C) Histogram of work function (Wf) values for the top-left image (Units in eV). (D) Histogram of work function (Wf) values for the top-right image (Units in eV) (see online version for colours)



3.3 Kelvin probe force microscopy

KPFM was performed on sample PMCD. The KPFM work function histograms represent a smaller range of work function values (Figure 3(C) and (D)) when compared with those of EF-PEEM. The former has a range from 3 eV to 5 eV whereas the latter ranges only from 4.31 eV to 4.7 eV. This might be explained by the fact that KPFM scans over smaller sections of the sample, typically 1–2 µm, accounting for localised variations, hence a narrower range of values. In the set of scans performed over different areas with KPFM, the range of work function values show little variation.

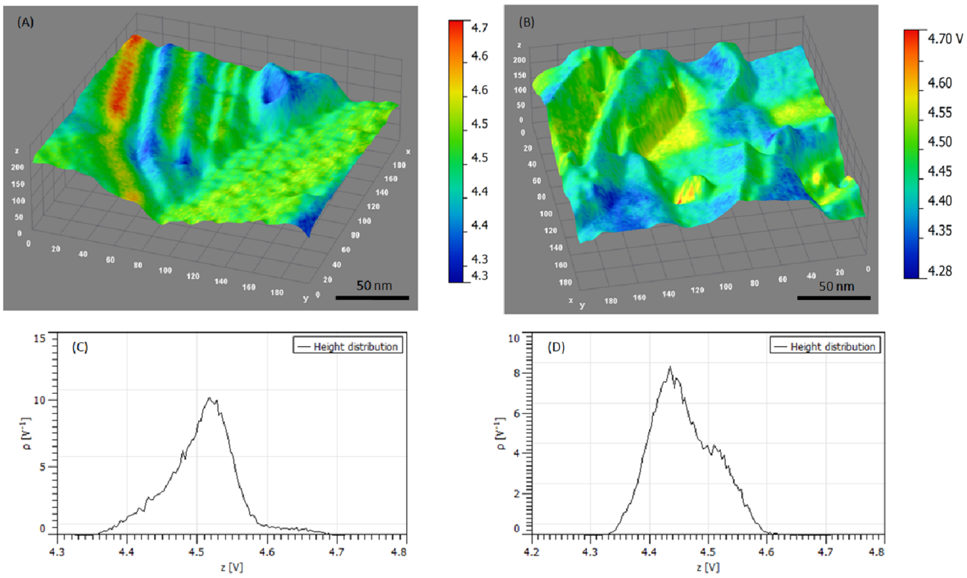
The histograms of the KPFM images show a peak at around 4.52 eV consistent with the data provided by the EF-PEEM (Figure 2). This observation indicates that the two techniques are able to produce work function data that may be directly compared.

The lateral resolution of KPFM is about 10 nm. As a result, KPFM scans can resolve the work function difference between differently oriented facets detailing important information about how the work function varies between them. This fact is illustrated in

Figure 3(A) where a crystalline step-like structure, a feature typical of polycrystalline, boron-doped diamond, is seen to be composed by different crystallographic planes. The image shows clear work function contrast between the different ridges of crystal facets as the pattern is repeated along the ridged structure. It was found that the work function variation between different facets was as large as 400 meV.

As well as CPD, KPFM maps the surface topography, so accurate information about the roughness and morphology of the sample is also obtained. In addition, it is also possible to precisely correlate topographical features as different microcrystals with work function variations.

Figure 3 (A) and (B) KPFM image of sample PCMD showing work function contrast of boron doped diamond with Li-O surface termination superimposed on a topographic plot of the same area. Note the clear correspondence between work function and crystal facets. (C) Histogram of work function (z) values for the top-left image (Units in eV). (D) Histogram of work function (z) values for the top-right image (Units in eV) (see online version for colours)



4 Conclusion

EF-PEEM and KPFM have been used to obtain visualisations of surface work function variations on lithium-oxygen functionalised semiconducting diamond films at different length scales. The results of preliminary studies conducted on boron-doped, *p*-type polycrystalline diamond have been presented.

The EF-PEEM images show that the surface functional coverage is not as uniform as desired. The functionalisation method used on the sample PCMD yields poor results as the surface work function is not uniform and spread on a wide range of values from 3.4 eV to 4.9 eV. On the other hand, the washing method used on PCMD2 produces a more uniform surface work function with a sharp peak at 4.05 eV within a narrower range of values.

The observed changes in work function across the polycrystalline diamond facets, as observed by KPFM, are believed to be attributed to localised changes in bulk conductivity due to the variation of doping concentration between crystals, surface defect density and the presence of non-diamond carbon on the surface. The histograms of work function obtained from both EF-PEEM and KPFM for the PCMD sample show consistent values and the same peak around 4.52 eV. So measurements from both techniques can be compared. The combined use of these two techniques is shown to be powerful: EF-PEEM is able to scan across large areas to provide a clear picture of the general state of the surface, while KPFM allows detail contained within individual crystal facets to be revealed. Future work will focus on the production and analysis of *n*-type and *p*-type diamond films with better control of surface morphology and bulk conductivity.

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